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REDETERMINATION OF CRYSTAL STRUCTURE OF ZINC THIOGALLATE

by

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REDETERMINATION OF CRYSTAL STRUCTURE OF ZINC THIOGALLATE

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ABSTRACT

Zinc thiogallate crystallizes in the tetragonal space group $I\bar{4}2m$ with a = 5.297(1), c = 10.363(1)A. In this space group zinc and gallium are disordered in the 4(d) sites. Most of the AGa_2X_4 compounds crystallize with the defect chalcopyrite, space group $I\bar{4}$ where the A and Ga ions are ordered and half of the A-sites are vacant. The result of this work indicates that disordering of Zn and Ga ions can occur and result in a structure with higher symmetry. All of these compounds transmit in the far infrared and are potential infrared window materials.
MATERIALS INDEX: $ZnGa_2S_4$; Disordered chalcopyrite

Introduction

Recently compounds with the composition AB_2X_4(A=Zn,Cd,Hg; B=Ga; X=S, Se,Te) have been studied because of their transmission in the far infrared and photoconductive and nonlinear optical properties (1-3). These compounds crystallize with the defect chalcopyrite structure which is derived from that of chalcopyrite by replacing half of the A-site cations by vacancies. Polycrystalline $ZnGa_2S_4$ was first synthesized by Hahn (4) and the results of the x-ray analysis were reported. The study indicated that the compound crystallized with the defect chalcopyrite structure with cell parameters a = 5.263, b = 10.42A; the space group was determined to be either $I\bar{4}$-S_4^2 or $I\bar{4}2m$-D_{2d}^{11}. Single crystals of this compound were first grown by Nitsche et al. by chemical vapor transport using iodine as the transport agent (5). The structure refinement for the assignment of space group $I\bar{4}$ reported a relatively large R-factor (6). In a recent study, single crystals of $ZnGa_2S_4$ of high quality were obtained and some of the physical properties were characterized (7). These crystals provided an opportunity to redetermine the structure with high accuracy, and the results of the structure refinement will be reported in this paper. The symmetry proved to be higher than for other compounds in this class.

Experimental

Crystals were grown by chemical vapor technique. Stoichiometric weights of elements were introduced into silica tubes which were then evacuated to 10^{-5} torr, and 5 mg/cc of iodine were added. The tubes were sealed off and enclosed in a tightly wound Kanthal coil to even out temperature gradients. The whole assembly was placed in a three-zone furnace and the crystal growth temperature program consisted of setting the furnace to back transport mode for one day, (growth zone at 1000°C and charge zone at 800°C). The furnace was equilibrated to the maximum reaction temperature (950°C) for three hours, and finally, the central zone was cooled to the growth temperature (910°C) at 1°C/hr. The transport process was carried out for ten days. Colorless crystals in the form of nearly regular tetrahedra of typical dimensions 1 x 1 x 1 mm were obtained. Powder x-ray diffraction indicated that it was pure $ZnGa_2S_4$ with cell parameters a = 5.296 and c = 10.368A.

A colorless transparent crystal (nearly regular tetrahedron) of zinc thiogallate was selected for the x-ray data collection on a Nicolet R3m/E diffractometer with graphite monochromatized MoKα radiation (0.71073A). The crystal was bounded by faces (1 −1 2), (1 1 −2), (−1 1 2), and (−1 −1 −2), each 0.0625 mm from the center of the crystal. Unit cell parameters were calculated by least-squares fitting to the positions of 25 reflections with 2θ between 25 and 35°. Three reflections were monitored every 97 reflections, with negligible change during the course of data collection. A complete sphere of reflections was collected up to $2\theta_{max}$ = 60°. Numerical absorption corrections were applied, based on the indexed and measured faces; minimum and maximum transmission factors were 0.181 and 0.280. Data were corrected for Lorentz and polarization effects. Intensities equivalent in Laue group 4/m were averaged, and eventually those equivalent in 4/mmm, to yield 247 unique observed reflections (not including space-group absences). All intensities measured were greater than 1.0σ. The known structure was refined in space group $I\bar{4}2m$. The parameters refined were 2 sulfur coordinates, 8 thermal parameters, a scale factor, an isotropic secondary extinction parameter, and a parameter η [final value 1.12(9)] that determines the absolute structure. Final R = 0.0300, *w*R = 0.0265 for 247 independent reflections with $w = 1/[s(F_0)^2 + 0.0002(F_0)^2]$, and S = 1.49. Maximum Δ/σ = 0.003 in final refinement cycle. The highest peak in the final difference map was 2.1, the deepest hole −4.0 eA^{-3}. The normal and anomalous scattering factors were taken from International Tables (8). All calculations were performed on a Data General Eclipse S140 computer using the SHELXTL 5.1 program package (9).

Discussion

Zinc thiogallate $ZnGa_2S_4$, tetragonal, space group $I\bar{4}2m$, a = 5.297(1), c = 10.363(1)A, Z = 2, μ(MoKα) = 146 cm^{-1}. Final S coordinates x=y=0.2563(1), z = 0.1187(1). Corresponding estimated standard deviations in the least significant digits are shown in parenthesis. The bond angles are listed in Table 1. The thermal parameters are listed in Table 2. The crystal structure is shown in Fig. 1. The metal atoms are all on fixed special positions, and each is surrounded tetrahedrally by four sulfur atoms. The Zn/Ga(1)-S tetrahedron is nearly regular, while the Ga(2)-S is distorted. Each sulfur atom is tetrahedrally surrounded by one Ga(2) atom, two Zn/Ga(1) atoms and one vacancy. The Zn/Ga(1)-S bond length, 2.315(1)A, is intermediate between 2.35A of Zn-S observed in ZnS and 2.24A of Ga-S observed in Ga_2S_3. The Ga(2)-S bond length, 2.281(1)A, is shorter than Zn/Ga(1)-S and longer than Ga-S in Ga_2S_3. The vacancy-S distance is 2.201(1)A.

Table 1. Bond angles (deg.)

S-Zn/Ga(1)-S[a]	110.20(5)	a	1/2-x, 1/2+y, 1/2-z
S-Zn/Ga(1)-S[b]	108.03(5)	b	-x, 1-y, z
S-Ga(2)-S[c]	106.92(5)	c	-x, y, -z
S-Ga(2)-S[d]	114.70(5)	d	-x, -y, z
Zn/Ga(1)-S-Zn/Ga(1[e])	107.98(4)	e	y, x, z
Ga(2)-S-Zn/Ga(1)	107.44(3)		

Table 2. Anisotropic temperature factors ($A^2 \times 10^4$)

atom	$U_{11}=U_{22}$	U_{33}	$U_{23}=U_{13}$	U_{12}
Zn/Ga(1)	106(3)	111(3)	0	0
Ga(2)	107(3)	85(3)	0	0
S	108(4)	95(5)	-14(2)	6(2)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(h^2a^{*2}U \quad + k^2b^{*2}U \quad +\ldots+ 2hka^{*}b^{*}U \quad)$

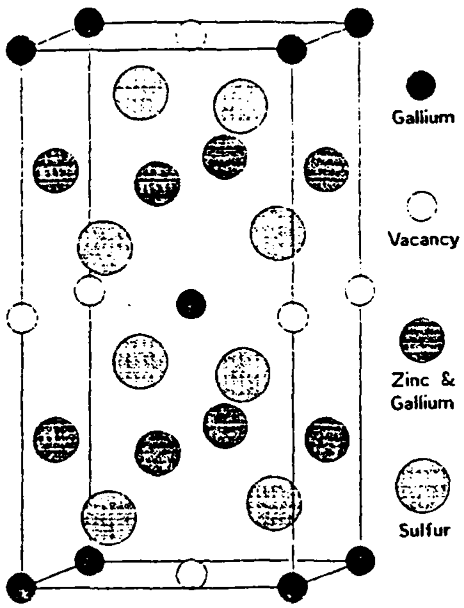

Fig. 1. Structure of $ZnGaS_4$

The typical structure of tetrahedral defect chalcopyrite structures with symmetry $I\bar{4}$ can be described in two ways, differing only in the choice of origin:

A in	2(a) 0,0,0	2(d) 0,1/2,3/4
B(1) in	2(b) 0,0,1/2	2(c) 0,1/2,1/4
B(2) in	2(c) 0,1/2,1/4	2(a) 0,0,0
X in	8(g) x,y,z;...	8(g) x,y,z;...
vac in	2(d) 0,1/2,3/4	2(b) 0,0,1/2

where vac indicates a vacant site. The origin of the second description is shifted relative to the first by the translation 0, 1/2, 1/4. These are equivalent descriptions, but the second was chosen in order to relate it more easily to the higher symmetry found in $ZnGa_2S_4$.

Initial refinement of the structure in $I\bar{4}$, using 429 reflections unique for Laue group 4/m, led to several features that indicated that the model was not completely satisfactory:

(1) The sulfur coordinates x = 0.2567 and y = 0.2560 were very nearly equal.

(2) The sulfur thermal parameters U_{11} = 0.0104 and U_{22} = 0.0107Å² were very nearly equal, as were the parameters U_{23} = 0.0017 and U_{13} = 0.0010Å².

(3) The distances Zn-S 2.313 and Ga(1)-S 2.317Å were nearly equal and different from Ga(2)-S 2.281Å.

(4) Refinement tended to oscillate unless appreciable damping was applied to the calculated least-squares shifts.

(5) The equivalent isotropic U values for Zn, 0.0109, and Ga(1), 0.0099Å², were possible more different than is physically reasonable.

These features suggested that the symmetry may be higher, namely, that of space group $I\bar{4}2m$. (The metal atom positions are fixed in either case, so cannot reveal the higher symmetry.) In this space group, atoms Zn and Ga(1) are required to be disordered in sites 4(d). Accordingly, refinement was attempted with 1/2 Zn + 1/2 Ga in positions 2(c) and 2(d), still in the second description of the structure in $I\bar{4}$. The weighted discrepancy wR decreased from 0.0272 to 0.0266 for 429 reflections and 19 parameters, and the equivalent isotropic U values became more nearly equal, 0.0104 for atoms in 2(d), and 0.0103Å² for atoms in 2(c). [Attempted variation of the fractions of Zn and Ga on these sites did not refine satisfactorily.]

Although no one of these features is overwhelming evidence of the higher symmetry, taken together they make a strong case that the complete symmetry is $I\bar{4}2m$. In this space group the structure is described as

A and B(1) in 4(d) 0, 1/2, 1/4; ...
B(2) in 2(a) 0, 0, 0
X in 8(i) x, x, z; ...
vac in 2(b) 0, 0, 1/2
with complete disorder of atoms A and B on site 4(d).

The structure refined smoothly in $I\bar{4}2m$, with no damping of the least-squares shifts. The final discrepancies were R = 0.0287 and wR = 0.0264 for

the 429 reflections used in the lower-symmetry refinement. This is essentially the same as from refinement in $I\bar{4}$, but the number of variable parameters has been reduced from 19 to 13.

Reflections equivalent in the higher symmetry Laue group 4/mmm were then merged to produce 247 independent observed reflections. Refinement of this structure gave final values of R = 0.0300 and wR = 0.0265 for 13 parameters, and the equivalent isotropic U values were similar for both metal sites, 0.0107 for atoms in 4(d) and 0.0099Å^2 for Ga(2) in 2(a). As a further test of this model, an alternative with complete disorder of the metal atoms over all six positions 4(d) and 2(a) was tested; the discrepancy indices were R = 0.0305 and wR = 0.0272. In addition, the thermal motion parameters differed more between the two sites, 0.0110 for atoms in 4(d) and 0.0093Å^2 for atoms in 2(a). Thus the model with Zn/Ga disorder confined to positions 4(d) is in best agreement with the diffraction data, and gives results that appear physically most reasonable.

Conclusions

Most of the AGa_2X_4 compounds crystallize with the defect chalcopyrite structure where the A and Ga ions are ordered. The space group is $I\bar{4}$. When there is a disordering between cations and vacancies as observed for the two phases $HgGa_2Te_4$, the space groups found were of higher symmetry, i.e. $F\bar{4}3m$ and $I\bar{4}2m$ (10). Agostinelli (11) reported a partial disordering between Co and Ga ions in α-$CoGa_2S_4$. The results of this work provide an example that disordering between A and Ga ions can occur and result in a structure with a higher symmetry.

Note: Since the completion of this study, the authors became aware of a similar structure study by C. K. Lowe-Ma and T. A. Vanderoh at the Naval Weapons Center, China Lake, CA whose work is being prepared for publication.

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